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(54) Title: PRINTING COMPOSITION

(57) Abstract: There is provided a coating composition for use in coating a diffraction grating, comprising metal pigment particles and a binder wherein the ratio of pigment to binder is sufficiently high as to permit the alignment of the pigment particles to the contours of the diffraction grating.

WO 2005/049745 A1

- 1 -

PRINTING COMPOSITION

The present invention relates to metal-based coating compositions. In particular, the present invention relates to such compositions for use in the coating of diffraction gratings in the production of holograms, such as holographic images and Diffractive Optically Variable Devices (DOVIDs)

Holograms are widely used for security authentication purposes, on items such as credit cards, currency, passports, vouchers, tickets and tamper-proof labels. Holograms are also used on packaging and gift wrap, for brand protection, decorative purposes and for consumer appeal. They are characterised by their ability to diffract incident light, rather than simply reflecting or absorbing light.

A number of hologram image styles are possible. The simplest, a uniform repeating pattern (URP) of a diffraction grating, is sometimes referred to as wallpaper. This gives a rainbow effect when incident light is diffracted. Dot matrix designs comprise many microscopic dots, each of them a separate diffraction grating. More complex holograms have three dimensional images, giving the impression of depth on a two dimensional surface. Stereograms are also possible, where two or more images are superimposed, giving the impression of movement as the image is viewed from different angles.

All of the above types of holograms require a microscopic diffraction grating pattern to be embossed onto a surface. The diffraction grating diffracts the light which is incident upon it, producing a rainbow effect or an image from the incident white light.

- 2 -

An original holographic image consists of a series of microscopic patterns, most commonly recorded on photosensitive material. From this original, a less fragile metal master copy is made, which has the recorded microstructure in surface relief. The master copy is used to make replicas, typically from nickel, followed by production copies, which can be used to emboss the design into a soft transparent surface, as a series of microscopic grooves. The most cost effective and common method of mass producing holograms involves the continuous embossing of the impression of the hologram into a substrate material, such as those described in US 4,913,858.

Typically, the diffraction grating is embossed into a thin layer of plastics, or a layer of resin coated onto a substrate. The plastics or resin may be either a thermosoftening material or a material that can be UV cured to harden it. While the former is more common, the latter tends to give a more durable and sharper emboss, which gives a brighter, clearer holographic effect.

The embossed plastic or resin subsequently needs to be coated in order to make the hologram clearly visible. Because plastics and resins have a low refractive index, they largely transmit the light that is incident upon them and reflect very little: typically only about 4% of the incident light. Hence the embossed hologram is very weak in intensity when viewed. To make the hologram clearly visible, it needs to be coated with a layer of reflective material. This can be either a metallic layer, which reflects 100% of the light incident upon it, or it can be a high refractive index (HRI) material, which reflects a lot of the

- 3 -

incident light and transmits the rest. Zinc sulphide is the most commonly used example of a HRI material.

This process of embossing the plastic or resin before application of the reflection enhancement layer is known as "soft embossing". There is an alternative process, "hard embossing", which creates the design by embossing into the substrate through the reflection enhancement layer. Here the substrate is usually a metallised plastics film or metallised paper, such as that described in JP 62/282078 A2.

Metallising the surface, to make a hologram visible, is usually done by vacuum metallisation, which involves evaporating molten metal under vacuum and depositing it onto a moving web of the desired substrate. Although metallisation is a fast process, the capital cost of the equipment is very high, resulting in limited availability. The hologram usually has to be transported to the vacuum metallisation equipment, so it is a separate process from the embossing step. It is desirable to be able to deposit the metal layer without using vacuum equipment. Another limitation is that the metal has to be deposited as a continuous film or in stripes; it is difficult to deposit the metal in a pattern. It is also desirable to be able to deposit the metal layer selectively over a hologram that does not cover the whole of the security document, packaging material or other product upon which holograms can be deposited.

There are two means of viewing a hologram. The first, white light transmission, requires the hologram to be illuminated from the opposite side to the viewer, so that the light travels through the hologram. The viewer therefore looks

- 4 -

through the hologram towards the light source. The hologram must be at least partly transparent, so it cannot be coated with a thick opaque layer of metal. The second, white light reflection, requires the hologram to be illuminated from the same side as the viewer. Obviously, for most applications such as for packaging and gift wrap or for viewing most security authentication holograms (for example on a passport), the hologram must be viewed from the same side as the incident light. Therefore, the hologram is viewed via white light reflection, with the viewer on the same side as the light source. In order to achieve this, one must also deposit a reflection enhancement layer. The reflection enhancement layer can be made of metal. Commonly, the hologram is metallised underneath the embossed layer, so that light passing through the hologram is reflected back to the viewer. In the case of non-transparent substrates such as paper, the metallised layer has to be on the upper, viewed surface; hence holograms on these substrates are produced by hard embossing through a metallised layer deposited on the upper surface of the substrate.

For many security applications, such as a hologram covering a signature in a passport, it is desirable to have a transparent or semi-transparent hologram, so that the substrate is visible through the hologram. One way of doing this is to metallise the embossed resin with a very thin layer of metal. The use of a thin layer of metal such as Cr, Te or Cu is proposed in US 4,856,857. However, these metals have high melting points and are difficult to evaporate; also, the thickness must be carefully controlled and this level of control is difficult to achieve using vacuum metallisation.

- 5 -

It is possible to replace the reflective metallised layer by a high refractive index (HRI) material, which causes some of the light to be reflected back to the viewer. The rest of the light passes through the high refractive index layer, allowing the substrate to be viewed at the same time. The most commonly used high refractive index material is zinc sulphide (such materials are described in US 5,513,019) because zinc sulphide is relatively easy to deposit under vacuum. It is, however, more expensive to deposit than metal. Zinc sulphide is water soluble, which can create problems in some applications. Thus, it is desirable to have a transparent hologram that is coated with metal rather than a HRI material.

Many applications require selective metallisation, for a holographic design that does not cover the whole of a substrate, but only selected areas. Either the whole, or part, of the substrate can be embossed. Only certain areas need to be metallised, so that only these areas will be visible as holograms. To date, the usual way of achieving this has been to metallise the whole of the embossed substrate by vacuum metallisation and then to etch away selected parts of the metal coating. Since aluminium is the most common material for metallisation, the de-metallisation step can be done using acid or alkali (such as sodium hydroxide), see for example US 2003/0223616 A1. The disadvantage of demetallisation is that an extra processing step is needed. Furthermore, there is a significant wastage of materials, adding to the cost of manufacture.

An alternative approach to selective metallisation is disclosed in US 6,440,277, where both the embossing and the localised metallisation are carried out under vacuum. Although this has the advantage of not requiring an extra

- 6 -

processing step, this technique suffers from the disadvantage that vacuum apparatus is required for both embossing and metallisation, which again, adds to the cost of manufacture.

US 5,786,910 describes a selective metallisation technique where the metallisation is produced in accurate register with the underlying hologram or diffraction pattern. This is achieved by printing oil in a pattern on the embossed substrate. Metal will not adhere to areas coated in oil during vacuum metallisation. Again, although the extra stage of a caustic treatment is not needed, this process also requires vacuum deposition equipment, adding to the cost of manufacture.

WO 93/23251 proposes an alternative to vacuum metallisation for selectively metallising a holographic image. The reflection enhancement layer is laid down on the embossed surface by printing a metallic coating, based on flake metallic pigment, from a standard printing press. However, the major disadvantage of this process is that the hologram can only be viewed from the non-metallised side of the embossed design. The metallic coating forms a thick layer which, when used underneath the embossed layer, allows the hologram to be viewed in white light reflection mode. When viewed with the metallised layer above the embossed layer, the hologram is not visible.

The use of a non-vacuum metallised metallic coating on top of an embossed hologram is disclosed in WO 98/18635 A. This document discloses a method of hard embossing, where a shim is impressed onto a substrate coated with metallic particles suspended in a binder. Optimum reflectivity is said to be achieved with

- 7 -

small, flat particles, such as aluminium flakes. WO 02/04234 A1 criticises the above patent, saying it is unworkable. Instead, WO 02/04234 A1 uses non-platelike deformable particles, such as spherical tin particles, in a coating on a surface which is subsequently hard embossed. Neither of these patents allows the hologram to be viewed from both sides.

The prior art therefore suffers from a number of disadvantages. In order to produce a hologram useful for commercial applications, it is desirable to:

- Produce the reflection enhancement layer by a simpler, cheaper method than vacuum metallisation
- Selectively metallise only chosen areas of the substrate
- Produce a reflection enhancement layer that allows the embossed hologram to be visible from both sides

It is an object of the present invention to overcome or alleviate one or more of the problems associated with the prior art.

Advantageously, it is also desirable to produce a hologram on transparent film, which can be viewed from either side of the film. Such a hologram would be very useful in security documents, such as banknotes, which incorporate a transparent polymeric "window". A device like this is extremely difficult to forge.

In accordance with a first aspect of the present invention there is provided a coating composition for use in coating a diffraction grating, comprising metal pigment particles and a binder wherein the ratio of pigment to binder is

- 8 -

sufficiently high as to permit the alignment of the pigment particles to the contours of the diffraction grating.

Thus, the composition of the present invention provides for the coating of a diffraction grating using a printing press which is faster and cheaper than conventional methods for depositing a metallised effect on a diffraction grating. Furthermore, owing to the ratio of pigment particles to binder, when using a translucent or transparent substrate, the image or pattern formed by the diffraction grating may be viewed from both sides of the substrate. Additionally, the quality of the lustre effect obtained using the compositions of the present invention is much improved compared with known metallised effects.

The applicants have found, surprisingly, that a hologram can be metallised in such a way that the holographic effect is visible from both sides, if it is printed with a metallic ink containing extremely thin metal flakes. The applicants have found that a coating composition according to the present invention can also be printed on the surface of the hologram. The metallic flakes of the present invention are substantially thin enough such that they can align with the contours of the embossed pattern and allow the pattern to be visible by making it reflective. In contrast thick metallic flakes will not do this, for example ball milled aluminium flakes and thicker vacuum metallised aluminium flakes.

In order to make the metallic flakes in the coating composition align with the embossed pattern, the applicants have found that the metal pigment particles need to be thinner than is usual for commercially available grades of vacuum

- 9 -

metallised pigments. The applicants have also discovered that the ratio in the coating composition of pigment to binder is important.

Thus, the composition of the present invention also provides for the coating of a diffraction grating using compositions of the present invention, where the composition is applied by a printing press. Application of the composition by printing press is faster and cheaper than conventional methods for depositing a metallised effect on a diffraction grating. Furthermore, when using a translucent or transparent substrate, the image and/or pattern formed by the diffraction grating may be viewed from both sides of the substrate. Additionally, the quality of the lustre effect obtained using the compositions of the present invention is much improved compared with known metallised effects.

The metallic pigment particles used in this invention may be prepared by vacuum deposition, such as the method described in US 4,321,087.

In one embodiment, the coating composition comprises metallic pigment particles, a solvent and a resin.

The metallic pigment particles may be metals, such as, for example, aluminium, gold, silver, platinum, copper or any other metal which may be deposited under vacuum. The particles may be an alloy, such as stainless steel, nichrome, brass, or any other alloy that may be deposited under vacuum. Preferably, the metallic pigment particles comprise aluminium.

The binder may comprise any one or more selected from the group comprising nitrocellulose, ethyl cellulose, cellulose acetate, cellulose acetate propionate (CAP), cellulose acetate butyrate (CAB), alcohol soluble propionate

- 10 -

(ASP), vinyl chloride, vinyl acetate copolymers, vinyl acetate, vinyl, acrylic, polyurethane, polyamide, rosin ester, hydrocarbon, aldehyde, ketone, urethane, polythyleneterephthalate, terpene phenol, polyolefin, silicone, cellulose, polyamide and rosin ester resins.

Preferably, the binder comprises 50% nitrocellulose 50% polyurethane. The composition may additionally comprise a solvent. The solvent may be ester/alcohol blends and preferably normal propyl acetate and ethanol. More preferably, the ester/alcohol blend is in a ratio of between 10:1 and 40:1, even more preferably 20:1 to 30:1.

The solvent used in the metallic ink may comprise any one or more of an ester, such as n-propyl acetate, iso-propyl acetate, ethyl acetate, butyl acetate; an alcohol, such as ethyl alcohol, industrial methylated spirits, isopropyl alcohol or normal propyl alcohol; a ketone, such as methyl ethyl ketone or acetone; an aromatic hydrocarbon, such as toluene; or water.

The average particle diameter may be in the range of 2 to 20 μ m. The average particle diameter is preferably in the range of 5 to 20 μ m, more preferably 8 to 15 μ m, even more preferably 9 to 10 μ m in diameter as measured by a laser diffraction instrument (Coulter LS130).

Preferably, the composition is used in the manufacture of a hologram.

In order that the hologram is clearly visible on both the first and second surface of a clear filmic substrate and the first surface of a paper substrate, preferably, the metallic pigment particles are printed in such a way as to align

- 11 -

themselves such that they follow and conform to the contours of the diffraction grating.

To accomplish this alignment of metal pigment flakes to the contours of the diffraction grating the coating composition preferably has a very low binder, a low pigment content and a high pigment to binder ratio and/or very thin pigment particles.

The coating composition preferably comprises low solids, high viscosity binders. Preferably, the pigment to binder ratio is in the range of 5:1 to 0.5:1 by weight. More preferably, the pigment to binder ratio is by weight in the range of 4:1 to 1:1, and even more preferably 3:1 to 1.5:1. Most preferably the pigment to binder ratio is 2.5:1.

The metal pigment content by weight of the composition may be less preferably less than 10%. Preferably the pigment content by weight of the composition is less than 6%, more preferably in the range of 0.1% to 6%, even more preferably in the range 0.1% to 3%, more preferably still in the range 0.2% to 2% by weight.

The compositions of the present invention can be applied to holograms for use on substrates such as security products, including identification documents like passports, identification cards, drivers licenses, or other verification documents, pharmaceutical apparel, software, compact discs, tobacco packaging and other products or packaging prone to counterfeiting or forgery, to protect them from fraudulent conversion, diversion or imitation.

- 12 -

Preferably, the thickness of the pigment particles in the composition when deposited on a diffraction grating is sufficiently thin as to permit the at least partial transmission of light therethrough. Consequently, the composition may be printed on substrate over a diffraction grating and the hologram may be visible through both the upper and lower surface of the substrate.

The thickness of the pigment particles may be less than 100nm. Preferably, the thickness of the pigment particles is less than 50 nm. More preferably, the thickness of pigment particle is less than 35 nm. More preferably still, the thickness of pigment particle is less than 20 nm. Even more preferably still, the thickness of pigment particle is in the range 5 – 18 nm.

In one embodiment, the thickness of the pigment particles is in the range 10 – 50 nm. In another embodiment, the thickness of pigment particle is in the range 10 – 30 nm. In another embodiment, the average thickness of pigment particle is 17 nm. In another embodiment, the average thickness of pigment particle is 12.5 nm.

Preferably, when the substrate carrying the metallised image or pattern is subsequently over-laid onto printed pictures and/or text, or the substrate is pre-printed with pictures and/or text and the metallised image or pattern is deposited thereon those pre-printed features are visible through the substrate and/or the metallic composition coated diffraction grating or image.

The coating compositions of the present invention may be deposited on a diffraction grating disposed on a substrate such as a substantially transparent,

- 13 -

translucent, or opaque substrate. The substrate may comprise paper, filmic material or metal, such as aluminium.

The substrate may comprise polymeric compounds. The substrate may comprise papers made from wood pulp or cotton or synthetic wood-free fibres.

The diffraction grating may be formed using any methods known to the skilled man such as those described in US 4,913,858 and US 5,164,227.

The composition of the present invention may be applied to the substrate by means of conventional printing press such as gravure, rotogravure, flexographic, lithographic, offset, letterpress intaglio and/or screen process, or other printing process.

Preferably, when the substrate carrying the enhanced diffractive image or pattern is subsequently over-laid onto printed pictures and/or text, or the substrate is pre-printed with pictures and/or text and the enhanced diffractive image or pattern is deposited thereon, those printed features are visible through the substrate and/or the metallic ink coated diffraction grating or image.

By varying the film-weight and density of the deposited metallic ink, the transmission of light through the enhanced image can be adjusted to provide a desirable range of visual effects.

The composition may further comprise modifying additives, for example colorants and/or suitable solvent(s).

Preferably, the resin maintains adhesion of the composition to the surface of the diffraction grating.

- 14 -

Specific additives can be added to the composition to modify its chemicals and/or physical properties. Polychromatic effects can be achieved by the introduction of transparent organic pigments and/or solvent soluble dyestuffs into the ink, to achieve a range of coloured shades.

The binder resins may be initially dissolved in the appropriate solvent(s) to form liquid varnishes. These varnishes can then be blended together with the metallic pigment and/or other components by means of a high-speed blender to produce the composition.

The composition may be formulated in to an ink.

In accordance with a further aspect of the present invention, there is provided a metallic ink comprising metal pigment particles and a binder wherein the ratio of pigment to binder is sufficiently high as to permit the alignment of the pigment particles to the contours of a diffraction grating.

Specific embodiments of the present invention will now be described, by way of example only, with reference to the following figures and examples, in which:

Fig.1 is an optical micrograph of a deposited coating composition in accordance with the present invention;

Fig. 2 is an optical micrograph of a deposited coating composition in accordance with the present invention; and

Fig. 3 is an optical micrograph of a comparative example of a deposited coating composition.

- 15 -

In one embodiment, the coating composition (the combination of pigment content, pigment to binder ratio and pigment flake thickness) should preferably be chosen such that the coverage of flakes on the diffraction grating suits the desired application. For example, for a hologram which is desired to be partly transparent, to enable the substrate to be viewed through the hologram, the flake coverage of the substrate may be less than 100%. A photomicrograph of a hologram of this type is shown in Fig. 1. The coating composition of Fig. 1 comprises pigment B (see table 1 hereinbelow), 1.5% pigment content by weight of composition and a pigment to binder ratio of 3:1 by weight. It can be clearly seen that all the flakes follow the contours of the emboss, although there are gaps between the flakes. 100% coverage of the grating using extremely thin flakes, which are in themselves partly transparent, would also give the same effect.

For a hologram of maximum brightness and intensity, the flake coverage ideally be 100% coverage of the substrate in a monolayer, without gaps between the flakes. A photomicrograph of a hologram of this type is shown in Fig.2. The coating composition of Fig. 2 comprises pigment D (see table 1 hereinbelow), 1.0% pigment content by weight of composition and a pigment to binder ratio of 1:1 by weight. All the flakes follow the contours of the underlying embossed diffraction grating.

If the coating composition is formulated so as to give flake coverage of the substrate that is more than a single layer, the flakes must necessarily overlap. This does not allow the overlying flakes to follow the contours of the diffraction grating, so the holographic effect is lost when viewing the face of the print. A

- 16 -

photomicrograph of a hologram of this type is shown in Fig.3. The coating composition of Fig. 3 comprises pigment B (see table 1 hereinbelow), 5% pigment content by weight of composition and a pigment to binder ratio of 0.3:1 by weight. Virtually all the flakes can be seen to be flat, without the embossed texture. Note that the reverse of the print will still show a good holographic effect, as the overlapping flakes form a mirror behind the diffraction grating.

Optical micrographs were taken using a Leitz Aristomet microscope at a magnification of x1000, using incident light and oblique illumination.

Example 1

A 12-micron thick transparent carrier film, two meters wide, made of polythyleneterephthalate was obtained from ICI Films, Wilmington, Del., USA (Melinex HS-2) was gravure coated with an acrylic resin, isobutyl methacrylate, obtained from DuPont (Elvacite 2045), and dried by means of hot air. In a second operation the acrylic-coated film was deposition coated with aluminium by means of a roll to roll vacuum chamber. The deposition rate and thickness of the vaporised aluminium layer over the printed acrylic coating were accurately controlled through continuous monitoring of the optical density during manufacture. The operating range of vacuum deposition was in the range 100 to 500 angstroms thick, the preferred thickness was in the range 190 to 210 angstroms thick. Several rolls were metallised at different thicknesses of aluminium, in order to give flake products of various thicknesses (see Table 1 below).

- 17 -

The aluminium layer was removed from the carrier film by means of dissolving the acrylic supporting layer in a bath containing ethyl acetate, releasing the aluminium layer from the carrier film. The resulting aluminium, in the form of a coarse flake in the resin solution, was then washed in a multi stage centrifuging process to remove the acrylic resin. The coarse aluminium flakes were mixed with ethyl acetate and disintegrated by a high shear mixing process to produce a controlled particle size distribution.

The suspension of vacuum metallised aluminium flakes in ethyl acetate was mixed with nitrocellulose and polyurethane resins and ethyl acetate to make a coating composition.

The coatings were printed on an RK proofer press over a polyester film embossed with a diffraction grating pattern.

The holographic intensity (colour and brilliance) of the face (printed side) and reverse (viewed through the film) of the print were judged on a scale of 1 to 10, where 1 is worst and 10 best.

The flake thickness of the vacuum metallised pigments varied, as shown in Table 1. Two aluminium flake pigments manufactured by ball milling were included for comparison.

Table 1

Pigment code	Pigment type	Flake thickness
A	Vacuum metallised aluminium	33nm
B	Vacuum metallised aluminium	25nm

- 18 -

C	Vacuum metallised aluminium	17nm
D	Vacuum metallised aluminium	12.5nm
E	Ball milled aluminium	120nm
F	Ball milled ("Silver Dollar" type) aluminium	300nm

Example 2 Effect of flake thickness

Pigments A, B, C & D were formulated into inks and printed onto film embossed with a diffraction grating, according to the method in Example 1. The quality of the resulting hologram was judged visually (Table 2).

Table 2

Pigment Code	Pigment loading	Pigment/Binder ratio (w/w)	Rating: reverse	Rating: face	
A	3.2%	2:1	3	1	
B	3.2%	2:1	4	2	
C	3.2%	2:1	7	4	
D	3.2%	2:1	9	4	

The thinnest flakes (product D) gave the best holographic effect, on both the face and the reverse of the prints.

Example 3 Use of ball milled flakes

The vacuum metallised pigments used in Example 2 were replaced by thicker ball milled pigments. The pigment content of the ink was adjusted to allow for the thicker pigments, which have a lower coverage. The visual rating of the holographic effect is shown in Table 3.

Table 3

Pigment Code	Pigment loading	Pigment/Binder ratio (w/w)	Rating: reverse	Rating: face	
E	16%	1.6:1	0	0	
F	16%	1.6:1	0	0	

The ball milled pigments did not give a suitable reflection enhancement layer on the reverse of the prints, because ball milled flakes are much less reflective than vacuum metallised pigments. The face of the prints appeared silvery, not holographic, since the flakes were too thick to follow the contours of the embossed layer.

Example 4 Effect of flake thickness with pigment surface area constant

The comparison of the effect of flake thickness shown in Example 2 was repeated, this time adjusting the pigment content according to the thickness of the flakes, to

- 20 -

gives a constant surface area of pigment per unit of ink. This means that each of the inks would have an equal ability to cover the substrate (table 4).

Table 4

Pigment Code	Pigment loading	Pigment/Binder ratio (w/w)	Rating: reverse	Rating: face	
B	3.2%	2:1	4	1	
C	2.2%	2:1	8	3	
D	1.6%	2:1	8	4	

As in Example 2, the thinnest flakes (product D) gave the best holographic effect on the face of the prints. Reducing the pigment content of the ink containing product D from that in Example 2 produced a better appearance of the face of the hologram, as the flakes were able to have monolayer coverage, without forming multi-layer stacks. However, the appearance of the reverse was not quite as good as at the higher pigment loading used in Example 2, because fewer flakes reduced the silver mirror effect.

Example 5 Effect of pigment to binder ratio

The thinnest flake (product D) was formulated into inks with different pigment to binder ratios, the pigment content being held constant. The visual ratings of the holographic effect are given in Table 5.

Table 5

Pigment Code	Pigment loading	Pigment/Binder ratio (w/w)	Rating: reverse	Rating: face	
D	1.5%	1:10	2	1	
D	1.5%	1:5	4	2	
D	1.5%	1:2	6	3	
D	1.5%	1:1	7	3	
D	1.5%	2:1	8	4	
D	1.5%	4:1	9	3	

The best holographic effect on the reverse of the prints was obtained with the highest pigment to binder ratio. The best holographic effect on the face of the prints was obtained at higher pigment to binder ratios, with an optimum between 1:1 and 4:1.

- 22 -

Example 6 Effect of pigment content

Pigment Code	Pigment loading	Pigment/Binder ratio (w/w)	Rating: reverse	Rating: face	
D	1.5%	1:1	7	2	
D	3%	1:1	9	4	
D	5%	1:1	10	1	

The highest pigment loading gave the best effect on the reverse of the print, due to the higher number of flakes giving a better reflective mirror. The best holographic effect on the face of the prints was at an intermediate pigment content, since too low a pigment content gives insufficient coverage and too high a pigment content gives overlapping flakes which do not follow the contours of the emboss.

- 23 -

CLAIMS

1. A coating composition for use in coating a diffraction grating, comprising metal pigment particles and a binder wherein the ratio of pigment to binder is sufficiently high as to permit the alignment of the pigment particles to the contours of the diffraction grating.
2. A composition as claimed in claim 1 wherein the composition further comprises a solvent.
3. A composition as claimed in claim 2 wherein the solvent comprises any one or more of the group comprising an ester, a ketone, an alcohol, an aromatic hydrocarbon and water
4. A composition as claimed in any one of claims 1, 2 or 3 wherein the metallic pigment particles comprise any one or more of the group comprising aluminium, gold, silver, platinum, copper, metal alloy, stainless steel, nichrome and brass.
5. A composition as claimed in any one of the previous claims wherein the binder comprises any one or more selected from the group comprising nitrocellulose, ethyl cellulose, cellulose acetate, cellulose acetate propionate (CAP), cellulose acetate butyrate (CAB), alcohol soluble propionate (ASP), vinyl chloride, vinyl acetate copolymers, vinyl acetate, vinyl, acrylic, polyurethane, polyamide, rosin ester, hydrocarbon, aldehyde, ketone, urethane, polyethyleneterephthalate, terpene phenol, polyolefin, silicone, cellulose, polyamide and rosin ester resins.

- 24 -

6. A composition as claimed in any one of the previous claims wherein the binder comprises 50% nitrocellulose and 50% polyurethane.

7. A composition as claimed in any one of the previous claims wherein the average particle diameter is in the range 2 - 20 μ m.

8. A composition as claimed in any one of the previous claims wherein the pigment to binder ratio is in the range of 5:1 to 0.5:1 by weight.

9. A composition as claimed in claim 8 wherein the pigment to binder ratio is by weight in the range of 4:1 to 1:1 by weight

10. A composition as claimed in claim 9 wherein the pigment to binder ratio is 2.5:1 by weight

11. A composition as claimed in any one of the previous claims wherein the metal pigment content by weight of the composition is less than 10%.

12. A composition as claimed in claim 11 wherein the pigment content by weight of the composition is less than 6%

13. A composition as claimed in claim 12 wherein the pigment content by weight of the composition is in the range of 0.2% to 6%.

14. . A composition as claimed in claim 12 wherein the pigment content by weight of the composition is in the range of 0.2% to 2%.

15. A composition as claimed in any one of the previous claims for use in coating a hologram.

16. A coating composition as claimed in any one of the previous claims wherein the thickness of the pigment particles is less than 100nm.

- 25 -

17. A coating composition as claimed in claim 16 wherein the thickness of the pigment particles is in the range 10 – 50 nm.

18. A coating composition as claimed in claim 17 wherein the thickness of the pigment particles is in the range 10 – 30 nm.

19. A coating composition as claimed in claim 16 wherein the thickness of the pigment particles is less than or equal to 35 nm.

20. A coating composition as claimed in claim 19 wherein the thickness of the pigment particles is in the range 5 – 35 nm.

21. A coating composition as claimed in claim 20 wherein the thickness of pigment particle is in the range 5 – 18 nm.

22. A metallic ink comprising metal pigment particles and a binder wherein the ratio of pigment to binder is sufficiently high to permit the alignment of the pigment particles to the contours of a diffraction grating.

1/2

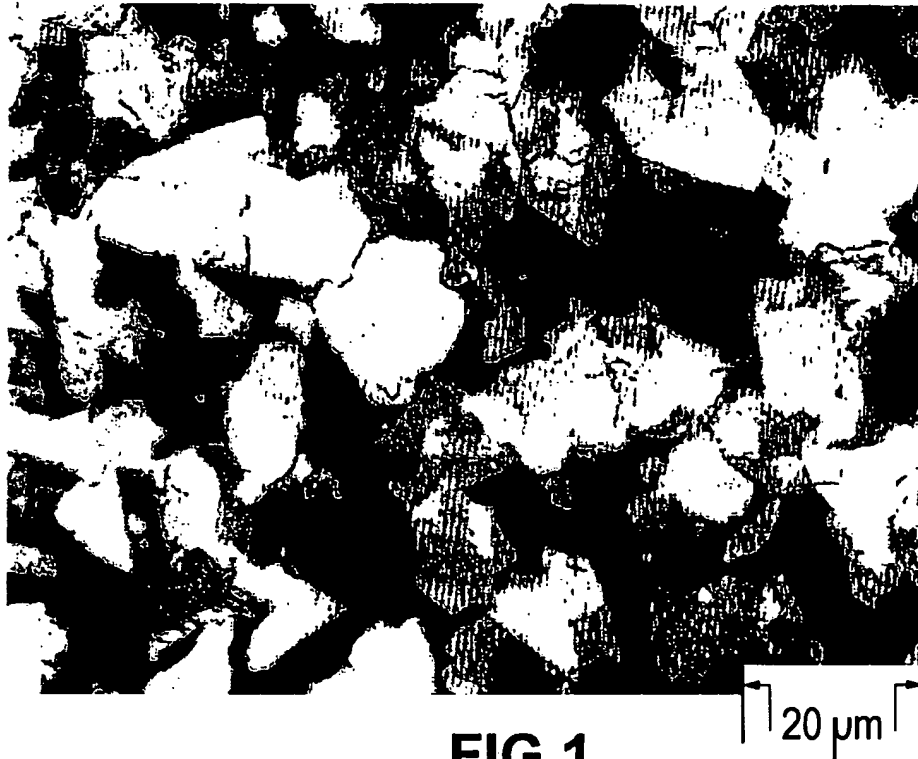


FIG.1.

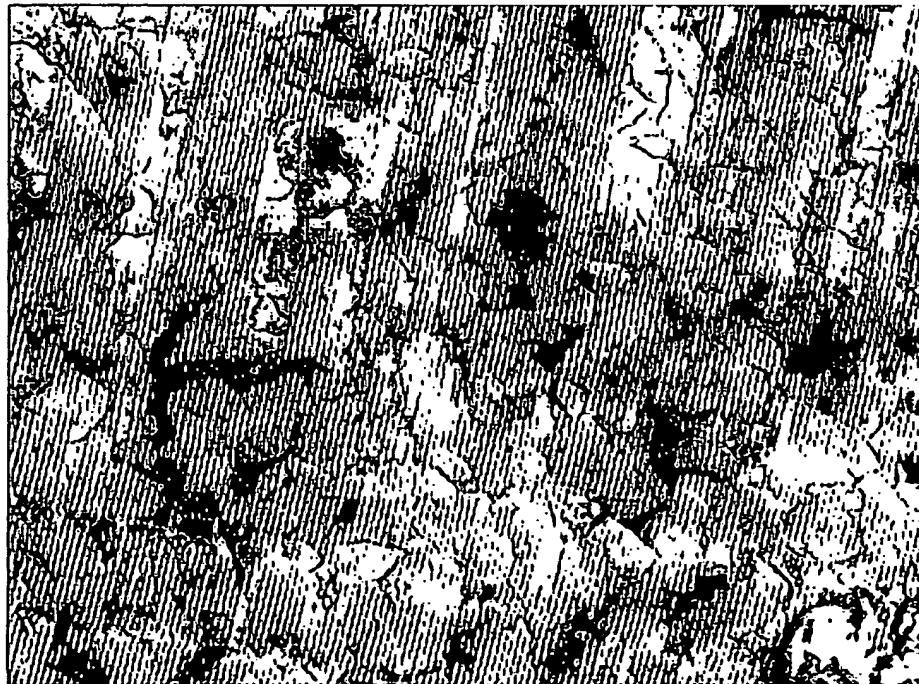


FIG.2.

2/2



FIG.3.

INTERNATIONAL SEARCH REPORT

International Application No

/GB2004/004805

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09D11/02 C09D11/00 C09D5/38 B42D15/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D B42D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 93/23251 A (AVERY DENNISON CORPORATION) 25 November 1993 (1993-11-25) cited in the application page 2, line 23 - page 3, line 8 page 6, line 17 - page 8, line 8 -----	1-22
X	WO 98/18635 A (DITTLER BROTHERS INCORPORATED) 7 May 1998 (1998-05-07) cited in the application page 4, line 17 - page 5, line 8 -----	1-22
X	WO 02/04234 A (DE LA RUE INTERNATIONAL LIMITED; MORRIS, ALAN; STONE, DAVID, ALLEN; DA) 17 January 2002 (2002-01-17) cited in the application page 3, line 18 - page 7, line 24 ----- -/--	1-22

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

10 February 2005

Date of mailing of the international search report

28/02/2005

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Vogel, T

INTERNATIONAL SEARCH REPORT

International Application No

GB2004/004805

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 990 682 A (NOF CORPORATION; BASF NOF COATINGS CO., LTD) 5 April 2000 (2000-04-05) abstract paragraphs '0025! - '0027! -----	1-22
X	US 5 672 410 A (MIEKKA ET AL) 30 September 1997 (1997-09-30) examples 12,13 -----	1-22
X	WO 95/17474 A (BASF CORPORATION; JOHNSON, DANIEL, W) 29 June 1995 (1995-06-29) the whole document -----	1-22

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB2004/004805

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: -

Present claims 1 and 22 relate to products defined by reference to a desirable characteristic or property, namely:
The ratio of pigment to binder should be sufficiently high as to permit the alignment of the pigment particles to the contours of the diffraction grating.

The claims cover all products having this characteristic or property, whereas the application provides support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT for only a very limited number of such products. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible.

Independent of the above reasoning, the claims also lack clarity (Article 6 PCT). An attempt is made to define the products by reference to a result to be achieved. Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope impossible. Consequently, the search has been carried out for those parts of the claims which appear to be clear, supported and disclosed, namely those parts relating to the products defined in the "preambles" of claims 1 and 22:

Claim 1: A coating composition comprising metal pigment particles and a binder.

Claim 22: A metallic ink comprising metal pigment particles and a binder.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

 In International Application No
 3B2004/004805

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